On the Reversible Addition of Alcohols to Nitriles Catalyzed by Sodium Ethylate, II

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DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

JULIA PEACHY HARRISON

BALTIMORE
June, 1912

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ACKNOWLEDGMENT.

The author wishes to take this opportunity to express her gratitude to President Remsen, Professor Morse, Professor Jones, Professor Bliss, Associate Professor Acree, and Associate Professor Lovelace for instruction and advice received both in the lecture room and the laboratory.

Special thanks are due to Associate Professor Acree at whose suggestion and under whose guidance this work was carried out and to Dr. E. K. Marshall, Jr., Carnegie Research Assistant, for valuable assistance.

On the Reversible Addition of Alcohols to Nitriles Catalyzed by Sodium Ethylate, II

Sodium ethylate has long been used as a catalyzer[1] in the inversion of menthone, in the acetoacetic ester synthesis and allied reactions, in the study of the reactions of alcohols with nitriles[2] by Nef, Stieglitz and Dains, and especially Stieglitz and McKee, and McKee, and of alcohols with mustard oils, acid chlorides, alkyl halides and in many other cases. The *quantitative* study of the mechanism of these reactions is of the greatest importance not only to the organic chemist but to all other chemists. In connection with other investigations along these lines I have taken up the *quantitative* study of the addition of alcohols to nitriles in order (1) to learn whether the reactions are reversible and to measure the equilibrium points, and (2) to study the exact nature of the mechanism of the action of sodium ethylate, and other ethylates, especially in the light of the other work with ethylates, phenolates, etc., which has shown that

[1] Vorländer: Ber. d. chem. Ges., **36,** 268. Karl Elbs: Kohlenstoff-Verbindungen, **1889,** p. 34. Marshall and Acree: Am. Chem. J., **49,** 130. Hofmann: Ber. d. chem. Ges., **2,** 120; **3,** 772. Bamberger: *Ibid.*, **15,** 2164. Schiff: *Ibid.*, **9,** 1316. Wurtz: Ann. chim. phys., [3] **42,** 43. Kremann: Monats. Chem., **26,** 783; **29,** 23. Claisen: Ber. d. chem. Ges., **20,** 646. Kossel, Krüger and Obermüller: Z. physiol. Chem., **15,** 321; **16,** 153. Purdie: J. Chem. Soc., **39,** 344; **47,** 863, 867; **59,** 469. Friedländer and Mähly: Ann. Chem. (Liebig), **229,** 210.

[2] Nef: Ann. Chem. (Liebig), **287,** 280. Dains: J. Am. Chem. Soc., **21,** 136. McKee: Am. Chem. J., **26,** 209; **36,** 209; **42,** 1.

the reaction velocities can be expressed as functions of the concentrations of both the ethylate ions and the nonionized sodium ethylate.

In another article[1] it was shown that in every case studied the reaction

$$RC \vdots N + C_2H_5OH \rightleftarrows RC(:NH)OC_2H_5$$

does not take place appreciably of itself, but, when catalyzed by ethylates, is reversible. The equilibrium point is the same whether measured from the nitrile or from the imido ester, although slow disturbing side reactions make the agreement in some cases less satisfactory than desired. The equilibrium point varies very widely with the different compounds. The per cent. of imido ester formed is illustrated by the following examples: butyronitrile, 0.90; propionitrile, 1.75; acetonitrile, 2.50; *p*-tolunitrile, 6.8; benzonitrile, 14.0; *p*-chlorobenzonitrile, 25.85; *p*-bromobenzonitrile, 27.2; *m*-bromobenzonitrile, 38.5; *p*-nitrobenzonitrile, 62.0; *m*-nitrobenzonitrile, 78.0; diisoamylcyanoamide, 98.0. The equilibrium point varies rather widely in some cases with changes in the concentrations of the nitrile and the ethylate, but fluctuates very little in other examples. Different ethylates catalyze the reaction with different velocities and the equilibrium points also often vary in such cases. The velocity of the reaction varies greatly with the different nitriles, the *p*-nitrobenzonitrile and chloroacetonitrile reacting very rapidly, whereas *o*-tolunitrile hardly adds alcohol at all.

With this point settled, *I turned my attention to the question whether the sodium ethylate reacts catalytically through the influence of the ethylate ions, or the nonionized sodium ethylate, or both.* This problem and analogous ones are of all the more interest because the sodium ethylate acts catalytically in the older sense in that it brings about its chemical changes by its mere presence and is not appreciably changed in its activity, whereas in the reactions with alkyl halides the sodium ethylate is entirely transformed into the end products. It was all the more desirable to study

[1] Marshall and Acree: Am. Chem. J., **49**, 127.

this and other similar reactions, therefore, to connect these limiting cases in which, on the one hand, the catalyzer is apparently not changed at all, with those in which, on the other hand, it is completely decomposed. It is of the highest importance that we have connected these limiting cases experimentally and shown that fundamentally there is no primary difference in the mechanism of the action of sodium ethylate in the two cases, the *apparent* dissimilarities really depending on a secondary factor, the stability or neutrality of intermediate products, and the tendency of the particular solution to yield the most nearly neutral system. This can be illustrated readily in such equations as the following:

$$\left\{\begin{array}{l} C_2H_5\overline{O} + IC_2H_5 \rightleftarrows C_2H_5\overline{O}.IC_2H_5 \longrightarrow \overline{I} + (C_2H_5)_2O \\ C_2H_5\overline{O} + CH_3C : N \rightleftarrows CH_3C(:\overline{N})OC_2H_5 + C_2H_5OH \longrightarrow \\ \qquad\qquad CH_3C(:NH)OC_2H_5 + C_2H_5\overline{O} \end{array}\right.$$

$$\left\{\begin{array}{l} C_2H_5ONa + IC_2H_5 \rightleftarrows C_2H_5ONa.IC_2H_5 \longrightarrow NaI + (C_2H_5)_2O \\ C_2H_5ONa + CH_3C : N \rightleftarrows CH_3C(:NNa)OC_2H_5 + \\ \qquad\qquad C_2H_5OH \longrightarrow CH_3C(:NH)OC_2H_5 + NaOC_2H_5 \end{array}\right.$$

Stieglitz and Schlesinger[1] have studied, in aqueous solutions, the reverse of this reaction, the decomposition of imido esters, in the presence of barium hydroxide as catalytic agent. They followed the ideas of Arrhenius,[2] Ostwald,[3] van't Hoff,[4] Warder,[5] Reicher,[6] Spohr,[7] Hemptinne,[8] Lö wenherz,[9] and others, who had shown that ordinary esters are saponified by bases (and acids) with a velocity approximately proportional to the concentration of the hydroxyl[10] (and hydrogen) ions. As

[1] Am. Chem. J., **39,** 719 (1908).
[2] Z. physik. Chem., **1,** 110 (1887).
[3] J. prakt. Chem., [2] **28,** 449 (1883).
[4] Etudes de dynamique chimique.
[5] Am. Chem. J., **3,** 340 (1882).
[6] Ann. Chem. (Liebig), **228,** 257 (1885).
[7] Z. physik. Chem., **2,** 194 (1888).
[8] *Ibid.*, **13,** 561 (1894); **31,** 35 (1899).
[9] *Ibid.*, **15,** 395 (1894).
[10] Miss Marion Brown is now engaged on the analogous study of the saponification of thioesters by sodium, potassium, lithium, ammonium, etc., sulphydrates in absolute ethyl alcohol in order to learn whether both the ionized and nonionized sulphydrates react with the thioesters. The much smaller ionization of these salts in alcohol will allow us to measure the possible activity of the nonionized sulphydrates much better than can be done in aqueous solutions in which the concentration of the nonionized sulphydrate is much smaller than in alcoholic solutions of the same concentration.

a result of their very fine experimental work, they came to the conclusion that an imido ester is decomposed completely into a nitrile and an alcohol *with a velocity proportional to the concentration of the hydroxyl ions and anions of the imido ester.* Stieglitz has apparently[1] overlooked a principle brought out by Professor Acree, namely, that the *nonionized compounds*, such as barium hydroxide and barium imido ester salts, may be concerned in such reactions. It can be shown that Stieglitz's excellent work harmonizes better with our theory than with his, and that our work, in which we can more accurately measure tall he necessary data, leads to the belief that he has perhaps interpreted his experiments unfortunately in that he did not consider the fact that BOTH *the nonionized barium hydroxide and the hydroxyl ions, and nonionized and ionized imido ester salts, may be concerned in the reaction.*

Before my own work was undertaken Professor Acree and Dr. Myers examined Stieglitz's data and saw that we secure constants just as good as his if we assume that $K_i = K_m$ for barium hydroxide and that a *gram molecule of nonionized barium hydroxide is just as effective in decomposing imido esters as is a gram ion of hydroxyl ions.* The reasons for the apparent equal validity of these two different interpretations of the experimental work of Stieglitz and Schlesinger is that in the solutions studied the barium hydroxide is so nearly completely ionized, 93 to 97.5 per cent., that the small influence of the nonionized portion, 2.5 to 7 per cent., is masked by the experimental errors necessarily involved in even this fine work. These uncertainties are apparent when we see that the widest variation in K_V in a given series sometimes becomes as high as 23 and 25 per cent., as in Tables XXV*b* and XV*b*, and averages about 9 per cent. for all of the series.

In the following tables I have given the essential details of Tables XX, XXIV, XXVIII, XXXII and XXXVI in Schlesinger's article. In the first column are given the concentrations of barium hydroxide used, in the second the value of K_V, in the third the value K_{OH}, or K_i, obtained by

[1] Am. Chem. J., **39**, 403. J. Am. Chem. Soc., **34**, 1688, 1689, 1690, 1694.

Schlesinger, in the fourth the deviation of each number in Column 3 from the mean of the entire column, in the fifth the constants calculated simply from the concentration of the barium hydroxide on our assumption that perhaps $K_i = K_m$, and in the sixth the deviation of each number in Column 5 from the mean of the entire column. I did not take the trouble to refer the constants in Column 5 to the same units used by Schlesinger but give simply the quotients of corresponding numbers in Columns 1 and 2. The errors involved in the two methods of calculation, as shown in Columns 4 and 6, are the points of real interest.

Table XX

Conc. of $Ba(OH)_2$	K_V	K_i Schlesinger	Error in per cent. Schlesinger	K_n	Error in per cent.
5.90	102	0.887	+3.86	17.28	+5.56
5.80	100	0.885	+3.75	17.24	+5.31
11.40	193	0.873	+2.23	16.93	+4.03
12.00	203	0.871	+1.99	16.91	+3.91
31.80	511	0.837	—1.99	16.07	—1.83
31.10	497	0.833	—2.46	15.98	—2.38
46.60	742	0.840	—1.64	15.92	—2.75
(48.00)	(741)	(0.812)	(—4.92)	(15.44)	(—5.69)
70.20	1090	0.835	—2.23	15.53	—5.13
70.60	1090	0.830	—2.81	15.44	—5.69
		0.854		16.37	

Table XXIV

Conc. of $Ba(OH)_2$	K_V	K_i Schlesinger	Error in per cent. Schlesinger	K_n	Error in per cent.
35.90	205	0.298	—0.67	5.71	—0.175
35.70	202	0.298	—0.67	5.66	—1.049
52.20	299	0.301	+0.33	5.73	+0.175
53.50	310	0.290	—3.33	5.79	+1.223
70.10	401	0.307	+2.33	5.72	±0.000
70.40	402	0.307	+2.33	5.71	—0.175
		0.300		5.72	

Table XXVIII

Conc. of $Ba(OH)_2$	K_V	K_i Schlesinger	Error in per cent. Schlesinger	K_n	Error in per cent.
30.50	152	0.255	+6.69	4.98	+9.45
30.70	171	(0.285)	....	....	....
61.50	255	0.220	—7.90	4.54	—0.22
64.30	291	0.241	+0.83	4.55	0.00
45.60	207	0.339	0.00	4.15	—8.79
46.20	210	0.239	0.00	4.53	—0.43
		0.239		4.55	

Table XXXII

Conc. of $Ba(OH)_2$	K_V	K_i Schlesinger	Error in per cent. Schlesinger	K_n	Error in per cent.
30.90	67.6	0.114	0.00	2.19	+0.92
32.20	67.5	0.109	—4.38	2.10	—3.22
46.20	101	0.115	+0.88	2.19	+1.38
46.50	109	0.123	+7.90	2.34	+7.83
61.50	130	0.113	—0.88	2.11	—2.76
61.60	128	0.111	—2.63	2.08	—4.15
		0.114		2.17	

Table XXXVI.

Conc. of $Ba(OH)_2$	K_V	K_i Schlesinger	Error in per cent. Schlesinger	K_n	Error in per cent.
32.70	510	1.62	+0.62	15.6	+1.30
43.70	690	1.66	+3.11	15.8	+2.60
62.50	930	1.55	—3.72	14.9	—3.25
		1.61		15.4	

When these tables are inspected it is seen that the errors in Columns 4 and 6 are uniformly of the same magnitude. Table XX is the least satisfactory one given by Schlesinger, the variations in a given series amounting to 25 per cent. in some cases. If Table XX is omitted, the average of all the values given in Column 4 is 2.14 per cent., while that of Column 6 is identically the same. If Table XX is included, the average of Column 4 is 2.25 per cent. and that of Column 6 is 2.71 per cent. When we recall that the average maximum variation of the constants in a series is 9 per cent., it is seen that

this difference between 2.71 per cent. and 2.25 per cent. is well within the experimental errors. I could be as fully justified, therefore, in believing that barium hydroxide acts through *both* its nonionized form and the hydroxyl ions, as are Stieglitz and Schlesinger in using the theory that the imido esters are decomposed by hydroxyl ions alone in a way shown by Arrhenius, Ostwald, and others to hold for ordinary esters, and my work on the ethylates presented in the following paragraphs leaves no doubt that my point of view is preferable.

For this reason I have chosen alcohol for use as the solvent, whenever possible, for studying reactions; the nonionized salt is present in much larger concentrations and its influence can be measured with much greater accuracy. My own work in alcoholic solutions has shown that the velocity of decomposition of imido esters is a function of the concentrations of *both* the ethylate ions and the sodium ethylate molecules, the values $K_i : K_m = 0.1172 : 0.0976$ and $K_i : K_m = 0.344 : 0.228$ having been found for benzimido ethyl ester and acetimido ethyl ester, for example. I consider that, in this case, as in others, sodium, potassium and other ethylates are *bases* in ethyl alcohol analogous to the corresponding hydroxides in water. If I were to work with sodium ethylate solutions more dilute than 0.002 N, the per cent. of ionization of the ethylate would be found to be above 90 per cent., and, as in Stieglitz's work with barium hydroxide, the reaction velocities would be so nearly proportional to the concentration of the ethylate ions that the activity of the sodium ethylate molecules would be masked by experimental errors to just the same extent observed in the work of Stieglitz and Schlesinger with barium hydroxide. Fortunately I can work with solutions as concentrated as 0.25 N, in which the relative concentration of the ethylate ions is only about 30 per cent. and that of the nonionized sodium ethylate 70 per cent., and in which the change due to the molecules is about 20 times as large as in 0.002 N solutions and hence easily measured. This work shows the interpretation of Stieglitz to be *partially* correct in that it proves that imido esters are decomposed by

hydroxyl (and ethylate) ions, and further substantiates the still broader theory that both ions and nonionized compounds must be considered in the study of all reaction mechanisms.

If the rate of reaction of the imido ester, or of the nitrile, is practically zero in the *absence* of ethylates, and in their *presence* it is a function of the concentrations of both the ethylate ions and the nonionized sodium ethylate, the reaction velocity must be expressed by the equation,

$$\frac{dx}{dt} = K_i\,[K'_i\alpha + K'_m(1-\alpha)] \times C_{ethylate} \times (A_1 - x)$$
$$- K_2\,[K'_i\alpha + K'_m(1-\alpha)] \times C_{ethylate} \times (A_2 + x)$$

in which it is assumed that the concentration of the alcohol is practically a constant, involved in K_2, that α is the per cent. of ionization of the sodium ethylate, $C_{ethylate}$, that K'_i is the catalytic effect of the ethylate ions, that K'_m is the catalytic effect of the nonionized sodium ethylate, that A_1 is the original concentration of the imido ester, that A_2 is the original concentration of the nitrile, and that x is the change in concentration of the imido ester in the time t. The integral of this equation is

$$K_V = \frac{1}{t}\ln\frac{KA_1 - A_2}{KA_1 - A_2 - (K+1)x} =$$
$$(K_1 + K_2)[K'_i\alpha + K'_m(1-\alpha)] \times C_{ethylate}$$
$$[K_i\alpha + K_m(1-\alpha)] \times C_{ethylate}$$

in which

$$K = \frac{K_1[K'_i\alpha + K'_m(1-\alpha)] \times C_{ethylate}}{K_2[K'_i\alpha + K'_m(1-\alpha)] \times C_{ethylate}} = \frac{K_1}{K_2}, \text{ and}$$
$$K_i = K'_i\,(K_1 + K_2), \text{ and } K_m = K'_m(K_1 + K_2).$$

It is to be noted that in developing these equations I have assumed the ratios $K_i : K_m$, for the reverse reactions, to be constant, an assumption which leads to the conclusion that K must be constant. I actually find K to be constant within the experimental errors, and hence independent of the concentration of the sodium ethylate. I have developed similar equations to apply to those cases in which K varies. K_V should be constant with varying concentrations of nitrile and a constant concentration of sodium ethylate, provided

that no double compounds are formed, and the nitrile does not visibly alter the physical properties of the solutions. As a matter of experiment we find in Table XIX an increase of only 7.4 per cent. in K_V with an increase of 800 per cent. in the concentration of acetonitrile. I have therefore used only one concentration of nitrile, 0.250 N, in all of the quantitative studies. In the remainder of the article I shall use the expressions K_i and K_m instead of K'_i $(K_1 + K_2)$ and K'_m $(K_1 + K_2)$ merely for convenience. Having then obtained the different values K_V, K'_V, K''_V, for the different concentrations of sodium ethylate, $1/V$, $1/V'$, $1/V''$, etc., I need only multiply the different values of K_V by the values for the corresponding V to obtain a series of simultaneous equations:

$$K_n = K_i\alpha + K_m(1 - \alpha),$$
$$K'_n = K_i\alpha' + K_m(1 - \alpha'),$$
$$K''_n = K_i\alpha'' + K_m(1 - \alpha''), \text{ etc.,}$$

in which K_n, K'_n, K''_n, etc., given in Table XIX, represent the reaction velocities which would be found if the solution were *normal* with respect to sodium ethylate having the degree of ionization α, α', α'', etc. When these equations are solved I obtain in Table XX the values 0.344 and 0.228 for K_i and K_m for acetimido ethyl ester, which are constant within the experimental errors, the ratio $K_i : K_m$ being approximately 1.5. In Table X in the work on benzimido ethyl ester I find the values 0.1172 and 0.0976 for K_i and K_m. This is entirely in harmony with the work on the action of alkyl halides on sodium ethylate, on sodium phenolate and sodium 1-phenyl-3-thiourazole, in which it was found that the reaction velocities can be expressed as functions of the concentrations of the ions and of the nonionized salts. The ratios $K_i : K_m$ are 2.13, 2.81 and 2.41 for the reaction of sodium ethylate with methyl iodide, ethyl iodide and ethyl bromide, respectively. I have furthermore substituted the values 0.344 and 0.228 in the various equations, $K_n = K_i\alpha + K_m$ $(1-\alpha)$, $K'_n = K_i\alpha' + K_m$ $(1-\alpha')$, etc., corresponding to the different values of α, α', α'', etc., and have obtained values for "K_n calculated" which are shown in Table XXI to agree very closely

with the "K_n found" obtained experimentally. I may conclude then that, in some respects, sodium ethylate behaves toward the unsaturated nitriles, $CH_3C \vdots N$, just as it does towards the unsaturated alkyl halides, $CH_3I \equiv$, an unstable addition product probably being formed as an intermediary step in both cases on account of the unsaturated character of all these substances.

But I have fortunately been able to go one step further in this work. When we examine the above equations we see that we could look upon the reactions as an *acceleration* of the purely *ionic* reaction by another reaction which I have called the nonionic reaction, whose coefficient is K_m. This *salt effect* is a very important phase of reaction mechanisms, is not very well understood at present, and has been a subject of investigation in this laboratory in all of the quantitative studies with the urazoles, amides, ethylates, etc., etc., and it has furthermore received attention from a large number of other workers. Arrhenius[1] suggested that this salt effect is due to the ions of the salt, and Euler[2] believed that these ions change the ionization of water and hence influence the rate of those reactions in which water is one of the reacting constituents. Stieglitz has adopted these ideas and applied them to his fine imido ester work.[3] He thinks that he has found evidence for the support of their theories, especially the idea of Euler, and believes that the "salt effect" of the cation is chiefly only a change in the active mass, or per cent. of ionization, of the water. But it was shown in another article[4] that Stieglitz has perhaps made an unfortunate interpretation of his own experimental work. His experimental data have been recalculated and found to give a full and complete verification of our ideas of "salt catalysis" rather than of those of Arrhenius and Euler, and prove that the "salt effect" is chiefly the transformation of the nonionized imido ester salt, augmented by an "abnormal salt catalysis."

[1] Z. physik. Chem., **1**, 110 (1887).

[2] *Ibid.*, **32**, 357 (1900).

[3] Am. Chem. J., **39**, 437 (1908); **39**, 586; **39**, 719. J. Am. Chem. Soc., **32**, 222 (1910).

[4] Am. Chem. J., **48**, 369; **49**, 120.

$$C_6H_5C(:\overset{+}{N}H_2)OC_2H_5 + H_2O \longrightarrow$$

$$C_6H_5C(OH)(\overset{+}{N}H_3)OC_2H_5 \longrightarrow C_6H_5COOC_2H_5 + \overset{+}{N}H_4$$

$$C_6H_5C(:NH_2Cl)OC_2H_5 + H_2O \longrightarrow$$

$$C_6H_5C(OH)(NH_3Cl)OC_2H_5 \longrightarrow C_6H_5COOC_2H_5 + NH_4Cl$$

Starting from the idea that the "salt effect" may be due to another reaction involving nonionized complex compounds, perhaps in traces in some cases, we have developed the above equation, $K_n = K_i\alpha + K_m(1 - \alpha)$, to express such a reaction when the nonionized salt (*e. g.*, sodium ethylate) forms the nonionized complex, and also the alternate equation, $K_n' = K_i\alpha + K_m(\alpha^2/V)$ which applies if the *nonionized* complex compound is formed from the *anion and cation* together. It was shown in another paper[1] that the first equation applies in all cases whereas the second applies in only two cases, which may be due to *algebraical accidents*. It will now be shown that the first equation applies very closely in the present work, whereas the second equation leads to no constants at all.

Let us take the case of a solution of 0.25 N acetimido ethyl ester and 0.0625 N sodium ethylate for which I used the equation $K_n = K_i\alpha + K_m(1 - \alpha)$, and the found values $K_n = 0.2848$, $\alpha = 0.481$, $K_i = 0.344$ and $K_m = 0.228$. If the equation $K_n = K_i\alpha + K_m(\alpha^2/V)$ were true, then the addition of sodium iodide to this solution of sodium ethylate and imido ester should suppress the ionization of the sodium ethylate in accordance with the isohydric principle, which I have proven experimentally, and should therefore decrease the value of $K_i\alpha$. But the *decrease* in α, the concentration of the ethylate ion, is small in comparison with the *increase* in α/V, the concentration of the sodium cations. If, for instance, we were to add 7 equivalents of sodium iodide to 0.0625 N sodium ethylate and 0.25 N acetimido ethyl ester, the ionization of the sodium ethylate should change from that of a N/16 solution, 0.481, to that of a N/2 solution, 0.234, in accordance with the isohydric principle, and the value of $K_i\alpha$ would change from $0.344 \times 0.481 = 0.1655$ to $0.344 \times 0.234 = 0.0805$, a decrease of 51 per cent. But if we use

[1] Am. Chem. J., **48**, 376.

the calculated value, about 8, for K_m, the value of $K_m(\alpha^2/V)$ would change from 0.118 to $8 \times 0.234 \times 0.169 = 0.3164$, an increase of about 168 per cent. As a consequence, then, the value of K_n should *increase* from 0.2848 found to 0.3969, or 39 per cent., when 7 equivalents of sodium iodide are added. If the total change were one of the cations and anions together in one reaction, increased by the cations in another reaction, the rate, K_v, would change from 0.0178, found, for the 0.0625 N sodium ethylate alone, to about 0.0778, an increase of 337 per cent. by the 7 equivalents of sodium iodide. If the reaction were one of sodium ethylate molecules, increased by another reaction of the cations, the velocity would change from 0.0178 found for the 0.0625 N sodium ethylate alone, to 0.0690 in the presence of 7 equivalents of sodium iodide, *an increase of 288 per cent.* As a matter of fact it *decreases* to 0.2512, and no one of these three hypotheses holds in my work. I have also tried, without success, to apply the formulas $K_n = K_i\alpha + K_m$, $K_n = K_i + K_m(1-\alpha)$, to a number of cases. When I finally collect my experimental material I shall again consider all of these hypotheses.

But let us calculate what should be the change if the alternate theory holds, and the equation $K_n = K_i\alpha + K_m(1-\alpha)$ represents the true course of all the reactions studied, even when an *added* salt changes the reaction velocity through the so-called "salt catalysis." As stated above, the value of $K_i\alpha$ should be changed from $0.344 \times 0.481 = 0.1655$ to $0.344 \times 0.234 = 0.0805$, and the value $K_m(1-\alpha)$ should consequently be changed from $0.288 \times 0.519 = 0.118$ to $0.228 \times 0.766 = 0.1745$. K_n consequently should be changed from $0.344 \times 0.481 + 0.228 \times 0.519 = 0.2838$ to $0.344 \times 0.234 + 0.228 \times 0.766 = 0.2551$. I find actually experimentally 0.2512 which differs from this calculated value only 1.6 per cent. but differs by 58 per cent. from the 0.3969 calculated on the first of the three above assumptions. The same close agreement with our theory is found when varying mixtures of sodium ethylate and sodium iodide, and sodium ethylate and sodium bromide, are used, and we can therefore conclude *that in this case* the mysterious so-called

"salt catalysis" is nothing more than a change, produced by the added salt, in the concentrations of the reacting constituents, as demanded by the Arrhenius-Barmwater theory of isohydric solutions.[1]

It is clear then that we have secured some experimental evidence concerning the nature of the catalytic action of added salts in this case and four others and that we can explain the *chief part* of this salt catalysis *in all cases yet studied by us* on the *rational basis* of the transformation of a nonionized complex compound formed by the reaction of, for example, the imido ester and the nonionized catalyzer, or on the basis of the reaction of the *nonionized catalyzer* with the imido ester *directly*, without the assumption of the formation of a complex compound. In the case of sodium ethylate, sodium phenolate, sodium thiourazole, and imido ester salts, the nonionized salt is present in large amounts and disappears in the reaction with the alkyl halide or water, the addition products,

$$C_2H_5I.C_2H_5ONa,\ C_2H_5C(OH)(NH_3Cl)(OC_2H_5),\ \text{etc.},$$

perhaps, forming the intermediate steps. In the case of the *pure* catalysis of the imido ester, or nitrile and alcohol, by sodium ethylate the nonionized salt does not disappear in the reaction, and yet the "salt effect" is due *solely* to the increase in the concentration of the *nonionized* sodium ethylate, which is also approximately true in the above cases in which the nonionized compound disappears as a result of the reaction: there is, however, a small "abnormal salt effect" in these latter cases. In some other reactions as pointed out before, it may be found that the "salt catalysis" is produced on account of the formation of complex compounds, in *traces* in some cases, from certain constituents and *anions and cations together*, while in still other cases the salt catalysis may be due to the formation of other anions or cations, or nonionized complex salts, having reaction velocities greater or smaller than those of the original constituents. The formulas

$$C_6H_5C(:NH_2Cl)(OC_2H_5).KCl,\quad C_6H_5C(:NH_2Cl)(OC_2H_5).\overset{+}{H},$$

$$C_2H_5ONa.C_2H_5I.NaI \text{ and } C_2H_5ONa.IC_2H_5.\overset{+}{Na}$$

[1] Z. physik. Chem., **28**, 424 (1899). *Ibid.*, **45**, 557 (1903).

are illustrations of the idea. The variations of this central idea are manifold. The question then whether the *added salt* will *increase* or *decrease* the reaction velocity will naturally depend simply upon the relative magnitudes of K_i and K_m, or other constants involved. If, for instance, K_m is the larger, the addition of the *added or catalyzing salt increases* the reaction velocity because the increase in the concentration of the nonionized form of the reactive salt causes the increase in $K_m(1 - \alpha)$ to be larger than the attendant decrease in $K_i\alpha$. The added salt suppresses the ionization of the active salt, and *lowers* the reaction velocity when K_i is larger than K_m because the decrease in $K_i\alpha$ is then greater than the increase in $K_m(1 - \alpha)$. This last case corresponds to all the problems that we have yet studied and to our interpretation of Stieglitz's imido ester work. If $K_m = K_i$ the added salt cannot change the reaction velocity, unless for reasons other than the ones discussed here. There may be "abnormal salt effects" in many cases, some of which we are studying.

This idea of salt catalysis is far more fortunate than the *assumption* by Euler and Stieglitz that the added salt changes the active mass, or per cent. of ionization, of the water or alcohol to a considerable extent. All the evidence is against any such idea that the water can change more than a very few per cent. in ionization, and their theory is clearly wrong for the reasons pointed out in earlier articles.[1]

EXPERIMENTAL

Acetonitrile and Acetimido Ethyl Ester

The bath used in this investigation has already been described.[2] Its temperature was constant at 25° to within ±0°.005. The alcohol used was dehydrated by boiling it with lime. No alcohol was used which contained more then 0.06 per cent. water, and in general the amount of water was considerably less than this. The *acetimido ethyl ester hydrochloride* was prepared as already described in another article.[3] The solutions of sodium ethylate were prepared by dissolving

[1] See especially Am. Chem. J., **41**, 475; **48**, 369.

[2] H. C. Robertson, Jr.: Diss., Johns Hopkins Univ., **1910**.

[3] Marshall and Acree: Am. Chem. J., **49**, 146.

pure sodium in cold alcohol. The measurements of the velocity of the reaction were carried out as follows: A solution of the required strength of acetimido ethyl ester hydrochloride was made by weighing the substance, transferring it to a graduated flask, dissolving it in alcohol as quickly as possible, and diluting the solution to the mark at 25°. A solution of sodium ethylate was prepared having the required strength plus the amount necessary to liberate the free imido ester from its hydrochloride. Thus, if 0.25 N imido ester and 0.25 N sodium ethylate were required, equal volumes of a 0.5 N solution of imido ester hydrochloride and N solution of sodium ethylate were mixed. The time of mixing the two solutions was noted, and aliquot portions (10 or 20 cc.) were pipetted out at various intervals and titrated with standard hydrochloric acid. The equilibrium point was determined by two duplicate titrations after the solution had stood overnight or longer. The equilibrium point from the imido ester side did not correspond to that obtained by starting with the nitrile. This is due to three causes: (1) to a small amount of ammonium chloride present in the original imido ester hydrochloride, (2) to the decomposition of the solution of the imido ester hydrochloride into ortho-ester and ammonium chloride during the short time necessary for bringing it to 25° and diluting the solution, and (3) to the decomposition of the imido ester hydrochloride into acetamide and ethyl chloride during this short time. The ammonia thus formed when the sodium ethylate solution is added remains practically constant throughout the reaction. The concentration of the ethylate is not influenced by this, and as the values for x with varying t are obtained from the difference in the alkalinity of the solution, x is therefore not affected. The only error to be taken into consideration is the value of A, or the concentration of the imido ester. This can be corrected for by considering the equilibrium point obtained by starting with the nitrile as the true one. For instance, we see in Table I that with 0.25 N acetonitrile and 0.5 N, 0.25 N, 0.125 N, and 0.0625 N sodium ethylate an average of 1.73 per cent. imido ester is formed at equilibrium. If my value of A_1 is 12.50, I have

$12.50 \times 0.0173 = 0.21$ as the amount of imido ester which should be present in the solution at equilibrium. This would give me as the equilibrium value of x $12.50 - 0.21 = 12.29$, but the value found for x is 12.13. I have, therefore, a correction for the ammonia formed amounting to 0.16. This gives me as a correct value for A, $12.50 - 0.16 = 12.34$. The amount of ammonia varies somewhat, as would be expected, in the individual experiments, but on an average amounts to a little over one per cent. The correction for the change in concentration of the imido ester has been applied in all cases.

We first proved that the free imido ester does not decompose with any appreciable velocity unless catalyzed by the ethylate. A solution of the imido ester hydrochloride was treated with nine-tenths of the theoretical amount of ethylate and titrated from time to time.

Time	3.5 hrs.	4 hrs.	23 hrs.	29 hrs.	46 hrs.	9 days
Cc. 0.2 N HCl	9.77	9.70	9.71	9.70	9.71	9.31

The amount of change due to the *uncatalyzed*, or spontaneous decomposition of the free imido ester cannot produce any appreciable error in our constants. When portions of this solution were treated with N/8 sodium ethylate the imido ester was decomposed as usual.

Since the mass of the alcohol can be considered practically constant, we have a reversible monomolecular reaction expressed by the following equations:

$$\frac{dx}{dt} = K_1(A_1 - x) - K_2(A_2 + x)$$

in which A_1 is the original concentration of the imido ester, A_2 that of the nitrile, and x the concentration of the nitrile formed during the reaction. At equilibrium, we have

$$K = \frac{K_1}{K_2} = \frac{A_2 + x}{A_1 - x}$$

Substituting K for K_1/K_2 we get

$$\frac{1}{t} \ln \frac{KA_1 - A_2}{KA_1 - A_2 - (K+1)x} K_1 + K_2 = K_V.$$

Since $A_2 = 0$ in all my experiments, we can simplify the above expression and obtain

$$\frac{1}{t} \ln \frac{KA_1}{KA_1 - (K+1)x} = K_1 + K_2 = K_V$$

in which

$$K = \frac{x}{A_1 - x}$$

K_n is obtained by dividing K_V by the concentration, $1/V$, of the sodium ethylate. All concentrations in this work are those obtained *after mixing* the solutions. The two following tables on acetonitrile and sodium ethylate are taken from a previous article.[1]

Table I—0.25 N Acetonitrile and Sodium Ethylate

Conc. sodium ethylate	Per cent. imido-ester formed
0.5 N	1.68
0.25 N	1.80
0.125 N	1.64
0.0625 N	1.80
0.03125 N	1.60
0.015625 N	1.60
Average used =	1.73

Table II—Acetonitrile and Sodium Ethylate

Conc. aceto-nitrile	Conc. sodium ethylate	Per cent. imido-ester formed
0.5 N	0.5 N	1.44
0.25 N	0.25 N	1.80
0.125 N	0.25 N	2.48
0.0625 N	0.25 N	2.56

Table III—Ionization of Sodium Ethylate in Absolute Alcohol at 25°

V	α	$(1 - \alpha)$
1	0.148	0.852
2	0.234	0.766
4	0.312	0.688
8	0.393	0.607
16	0.481	0.519
32	0.577	0.423
64	0.686	0.314

[1] Marshall and Acree: Am. Chem. J., **49**, 149.

Table IV[1]*—0.25 N Acetimido Ethyl Ester and 0.25 N Sodium Ethylate*

$A_1 = 12.34$	$A_2 = 0$	$K = 55.1\ (57.8)$[2]
t	x	K_V
25	10.11	0.0689
31	10.71	0.0693
37	11.18	0.0689
46	11.61	0.0684
	12.13	
	Average	= 0.0689
	K_n	= 0.2756

Table V—0.25 N Acetimido Ethyl Ester and 0.25 N Sodium Ethylate

$A_1 = 12.05$	$A_2 = 0$	$K = 54.0\ (56.4)$
t	x	K_V
21	9.06	0.0691
28	10.15	0.0695
34	10.66	0.0680
40	11.04	0.0675
	11.84	
	Average	= 0.0685
	K_n	= 0.2740

Table VI—0.25 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 12.22$	$A_2 = 0$	$K = 60.0\ (57.2)$
t	x	K_V
5	1.98	0.0359
15	4.79	0.0339
27	7.10	0.0332
40	9.41	0.0382
91	11.41	0.0332
	12.01	
	Average	= 0.0341
	K_n	= 0.2728

[1] The values in Tables IV and V are not used in the final calculations because in these concentrations the abnormal physical properties become noticeable. Dr. Meyers has obtained similar results in his work on the addition of ethyl alcohol to *p*-bromobenzonitrile in the presence of sodium, potassium and lithium ethylates.

[2] The values of K given outside the parentheses in each of the following tables are those calculated from the data for the corresponding concentrations in Table I, the values inside the parentheses being derived from the *average used*, 1.73. The influence of K in the formula is so small that identically the same reaction velocity is obtained by the use of either value of K.

Table VII—0.25 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 12.30$	$A_2 = 0$	$K = 60.4\ (57.6)$
t	x	K_V
5	2.07	0.0375
15	5.03	0.0359
25	6.91	0.0339
40	8.96	0.0339
60	10.52	0.0341
90	11.53	0.0341
	12.09	

Average = 0.0349
K_n = 0.2792

Table VIII—0.25 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 12.23$	$A_2 = 0$	$K = 60.1\ (57.2)$
t	x	K_V
10	3.52	0.0345
17	5.20	0.0334
23	6.44	0.0334
31	7.70	0.0330
45	9.35	0.0334
60	10.46	0.0341
90	11.42	0.0336
	12.02	

Average = 0.0336
K_n = 0.2688

Table IX—0.25 N Acetimido Ethyl Ester and 0.0625 N Sodium Ethylate

$A_1 = 12.23$	$A_2 = 0$	$K = 54.7\ (57.2)$
t	x	K_V
15	2.90	0.0184
25	4.33	0.0179
35	5.51	0.0175
50	7.01	0.0175
66	8.23	0.0174
126	10.73	0.0177
147	11.10	0.0174
	12.02	

Average = 0.0177
K_n = 0.2832

Table X—0.25 N Acetimido Ethyl Ester and 0.0625 N Sodium Ethylate

$A_1 = 12.27$	$A_2 = 0$	$K = 54.8\ (57.4)$
t	x	K_V
25	4.39	0.0181
35	5.63	0.0180
45	6.66	0.0179
60	7.93	0.0179
80	9.15	0.0178
115	10.53	0.0179
∞	12.06	

Average = 0.0179
$K_n = 0.2864$

Table XI—0.25 N Acetimido Ethyl Ester and 0.03125 N Sodium Ethylate

$A_1 = 12.15$	$A_2 = 0$	$K = 59.7\ (56.9)$
t	x	K_V
15	1.53	0.00914
30	2.91	0.00928
45	4.04	0.00917
65	5.40	0.00924
90	6.74	0.00898
110	7.65	0.00930
156	9.13	0.00928
262	10.92	0.00937
∞	11.94	

Average = 0.00921
$K_n = 0.2947$

Table XII—0.25 N Acetimido Ethyl Ester and 0.03125 N Sodium Ethylate

$A_1 = 11.92$	$A_2 = 0$	$K = 58.5\ (55.8)$
t	x	K_V
25	2.44	0.00933
41	3.71	0.00928
56	4.72	0.00921
71	5.63	0.00924
92	6.68	0.00919
122	7.79	0.00898
∞	11.71	

Average = 0.00919
$K_n = 0.2941$

Table XIII—0.25 N Acetimido Ethyl Ester and 0.015625 N Sodium Ethylate

$A_1 = 24.44$	$A_2 = 0$	$K = 60.2\ (57.2)$
t	x	K_V
15	1.60	0.00477
30	3.11	0.00477
50	4.91	0.00479
80	7.50	0.00484
104	9.17	0.00479
210	15.03	0.00491
333	18.92	0.00500
∞	24.02	

Average = 0.00484
K_n = 0.3098

Table XIV—0.25 N Acetimido Ethyl Ester and 0.015625 N Sodium Ethylate

$A_1 = 24.36$	$A_2 = 0$	$K = 59.8\ (57.0)$
t	x	K_V
15	1.70	0.00489
30	3.30	0.00491
51	5.21	0.00481
90	8.29	0.00472
207	14.92	0.00474
292	17.82	0.00470
∞	23.94	

Average = 0.00479
K_n = 0.3066

Table XV—0.5 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 24.27$	$A_2 = 0$	$K = 66.4$
t	x	K_V
11	8.35	0.0382
17	11.87	0.0394
26	15.49	0.0389
33	16.70	0.0352
40	18.24	0.0348
60	21.12	0.0341
85	22.80	0.0329
∞	23.91	

Average = 0.0362
K_n = 0.2896

Table XVI—0.5 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 24.07$	$A_2 = 0$	$K = 66.0$
t	x	K_V
25	14.99	0.0401
32	16.59	0.0375
41	18.54	0.0371
53	20.37	0.0368
67	21.70	0.0368
∞	23.70	

Average = 0.0375
K_n = 0.3000

Table XVII—0.125 N Acetimido Ethyl Ester and 0.25 N Sodium Ethylate

$A_1 = 6.07$	$A_2 = 0$	$K = 39.5$
t	x	K_V
8	2.59	0.0719
16	4.00	0.0705
21	4.50	0.0679
27	4.99	0.0684
33	5.31	0.0689
41	5.54	0.0670
54	5.80	0.0721
∞	5.92	

Average = 0.0685
K_n = 0.2740

Table XVIII—0.0625 N Acetimido Ethyl Ester and 0.25 N Sodium Ethylate

$A_1 = 6.09$	$A_2 = 0$	$K = 37.1$
t	x	K_V
15	3.71	0.0661
21	4.43	0.0654
26	4.86	0.0658
32	5.22	0.0663
38	5.44	0.0654
45	5.67	0.0690
50	5.73	0.0672
∞	5.93	

Average = 0.0661
K_n = 0.2644

The concentrations in the above tables are all expressed after mixing. Referring the reaction velocities for the different dilutions to normal concentration, we obtain comparable values, which we shall designate K_n. The following table gives a résumé of all the above work and was used in calculating the values of K_i and K_m given in Table *XX*.

Table XIX—0.25 N Acetimido Ethyl Ester and Sodium Ethylate

Concentration of sodium ethylate	$K_1 + K_2 = K_V$		K_n
0.125 N	0.0341	0.0342	0.2736
	0.0349		
	0.0336		
0.0625 N	0.0177	0.0178	0.2848
	0.0179		
0.03125 N	0.00931	0.00920	0.2944
	0.00919		
0.015625 N	0.00484	0.00482	0.3084
	0.00479		

Acetimido Ethyl Ester and Sodium Ethylate

Concentration of imido ester	Concentration of sodium ethylate	$K_1 + K_2 = K_V$		K_n
0.5 N	0.125 N	0.0362	0.0369	0.2952
		0.0375		
0.5 N	0.25 N	....		0.2852[1]
0.25 N	0.25 N	0.0692		0.2768
0.125 N	0.25 N	0.0685		0.2740
0.0625 N	0.25 N	0.0661		0.2644

If, in this case of catalysis, we have both the ethylate ion and sodium ethylate molecules concerned in the reaction, we should be able to calculate the constant for the velocity of the ionic and molecular reactions separately, as has been done in the case of the reaction between ethylates and alkyl halides.[2] I have used the equation $K_n = K_i\alpha + K_m(1 - \alpha)$ in which K_i is the ionic velocity and K_m the molecular velocity, and calculated the following values for K_i and K_m, which are seen to be very constant.

[1] Recalculated from the data for 0.5 N imido ester and 0.125 N sodium ethylate.

[2] See other work by Robertson, Marshall, Harrison, Chandler, Myers, Shrader, Brown, Nirdlinger and Rogers: Am. Chem. J., **48**, 352; **49**, 116, 127.

Table XX

V	K_i	K_m
8 : 16	0.336	0.238
8 : 32	0.342	0.230
8 : 64	0.346	0.228
16 : 32	0.346	0.228
16 : 64	0.346	0.222
32 : 64	0.348	0.222
	Average, = 0.344	0.228

I have used the values $K_i = 0.344$ and $K_m = 0.228$ in recalculating the values of K_n corresponding to the different concentrations of sodium ethylate used, and have compared these values of "K_n calculated" with those of "K_n found." The agreement is quite satisfactory as can be seen from the following table:

Table XXI—0.25 N Acetimido Ethyl Ester and Sodium Ethylate

Concentration of sodium ethylate	K_n found	K_n calculated	Error in per cent.
0.125	0.2736	0.2736	±0.00
0.0625	0.2848	0.2838	+0.35
0.03125	0.2944	0.2949	—0.10
0.015625	0.3084	0.3076	+0.26
		Average error =	—0.05

After thus learning the effect of the *ethylate ion* and of the *nonionized sodium ethylate* on this reaction, I thought it wise to test this theory further by suppressing the ionization of the sodium ethylate by the addition of sodium iodide in order to see if the new reaction velocities correspond to the new ionization values. This should be the case if the added sodium iodide produces no "abnormal salt effect," the theory of which was discussed fully on page 15. The following tables show, in the main, that the change in the reaction velocity is very close to that calculated from our theory, and that the sodium iodide produces no appreciable "abnormal salt effect." The value of K used was determined experimentally in each case

by measuring the equilibrium point in the corresponding mixture of sodium iodide, sodium ethylate and acetonitrile.

Table XXII—0.25 N Acetimido Ethyl Ester, 0.25 N Sodium Ethylate and 0.25 N Sodium Iodide

$A_1 = 12.45$	$A_2 = 0$	$K = 124$
t	x	K_V
20	9.00	0.0656
26	10.08	0.0651
31	10.70	0.0650
37	11.22	0.0647
44	11.66	0.0654
	12.35	

Average = 0.0651
Calculated = 0.0638
K_V without sodium iodide = 0.0692

0.25 N Acetonitrile and 0.25 N Sodium Ethylate with 0.25 N Sodium Iodide.—Twenty cc. were taken for titration, and required 25.22, 25.24, 25.23 cc. 0.2 N hydrochloric acid. This corresponds to 0.84 per cent. imido ester present at equilibrium.

Table XXIII—0.25 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate with 0.125 N Sodium Iodide

$A_1 = 12.03$	$A_2 = 0$	$K = 119$
t	x	K_V
32	7.78	0.0329
45	9.13	0.0322
53	9.71	0.0318
61	10.23	0.0320
68	10.61	0.0322
76	10.91	0.0324
	11.93	

Average = 0.0322
Calculated = 0.0321
K_V without sodium iodide = 0.0342

0.25 N Acetonitrile and 0.1245 N Sodium Ethylate with 0.125 N Sodium Iodide.—Twenty cc. were used for titration, and required 12.73, 12.76 cc. 0.2 N hydrochloric acid. This

corresponds to 0.84 per cent. imido ester present at equilibrium.

Table XXIV—0.25 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate with 0.375 N Sodium Iodide

$A_1 = 12.25$	$A_2 = 0$	$K_V = 122$
t	x	K_V
21	5.97	0.0322
25.5	6.77	0.0320
30	7.41	0.0313
41	8.66	0.0304
48	9.37	0.0306
59	10.12	0.0304
69	10.61	0.0300
∞	12.15	

Average = 0.0310
Calculated = 0.0319
K_V without sodium iodide = 0.0342

0.25 N Acetonitrile and 0.1246 N Sodium Ethylate with 0.375 N Sodium Iodide.—Ten cc. were used for titration and required 6.34, 6.33 cc. 0.2 N hydrochloric acid. This corresponds to 0.84 per cent. imido ester present at equilibrium.

Table XXV—0.25 N Acetimido Ethyl Ester and 0.0625 N Sodium Ethylate with 0.0625 N Sodium Iodide

$A_1 = 12.14$	$A_2 = 0$	$K = 120$
t	x	K_V
16	2.98	0.0178
21	3.68	0.0174
27	4.38	0.0167
36	5.42	0.0166
51	6.86	0.0167
67	8.04	0.0164
108	9.99	0.0164
∞	12.04	

Average = 0.0169
Calculated = 0.0171
K_V without sodium iodide = 0.0178

0.25 N Acetonitrile and 0.616 N Sodium Ethylate with 0.0625 N Sodium Iodide.—Ten cc. were used for titration and re-

quired 3.22, 3.19, 3.20 cc. 0.2 N hydrochloric acid. This corresponds to 0.96 per cent. imido ester present at equilibrium.

Table XXVI—0.25 N Acetimido Ethyl Ester and 0.0625 N Sodium Ethylate with 0.1875 N Sodium Iodide

$A_1 = 12.20$	$A_2 = 0$	$K = 121$
t	x	K_V
16	2.81	0.0165
21	3.46	0.0160
34	4.94	0.0155
43	5.98	0.0162
61	7.43	0.0156
84	8.85	0.0156
126	10.41	0.0156
∞	12.10	

Average = 0.0159
Calculated = 0.0165
K_V without sodium iodide = 0.0178

0.25 N Acetonitrile and 0.0626 N Sodium Ethylate with 0.1875 N Sodium Iodide.—Ten cc. were used for titration and required 3.24, 3.26 cc. 0.2 N hydrochloric acid. This corresponds to 0.96 per cent. imido ester present at equilibrium.

Table XXVII—0.25 N Acetimido Ethyl Ester and 0.0625 N Sodium Ethylate with 0.4375 N Sodium Iodide

$A_1 = 12.10$	$A_2 = 0$	$K = 120$
t	x	K_V
20	3.33	0.0162
27	4.26	0.0162
34	5.03	0.0160
42	5.79	0.0157
50	6.48	0.0155
69	7.79	0.0152
81	8.52	0.0153
∞	12.00	

Average = 0.0157
Calculated = 0.0160
K_V without sodium iodide = 0.0178

0.25 N Acetonitrile and 0.0634 N Sodium Ethylate with 0.4375 N Sodium Iodide.—Twenty cc. were used for titra-

tion and required 6.44, 6.43 cc. 0.2 N hydrochloric acid. This corresponds to 0.74 per cent. imido ester at equilibrium.

In the following table I give a résumé of all the above work on the *salt catalysis* produced by sodium iodide.

Table XXVIII—0.25 N Acetimido Ethyl Ester, Sodium Ethylate and Sodium Iodide

Concentration of sodium ethylate	Concentration of sodium iodide	K_V found	K_V calculated	Error in per cent.
0.250 N	0.250 N	0.0651	0.0638	+2.0
0.125 N	0.125 N	0.0322	0.0321	+0.3
0.125 N	0.375 N	0.0310	0.0319	—3.0
0.0625 N	0.0625 N	0.0169	0.0171	—1.2
0.0625 N	0.1875 N	0.0159	0.0165	—3.8
0.0625 N	0.4375 N	0.0157	0.0160	—1.9

Average error = —1.26

The experiments show very clearly that the "salt effect" produced by the added sodium iodide can be interpreted as due *chiefly* to the change in ionization of the sodium ethylate by the sodium iodide and the resulting change in reaction velocity.

Since the acetimido ethyl ester decomposes so nearly completely into acetonitrile and alcohol in the presence of sodium ethylate, I made some calculations to see whether good constants can be obtained by considering the reaction as monomolecular and considering A to be the total change in the concentration of the imido ester. The following corrected tables show that the constants have practically the same value whether calculated in this way or on the correct basis:

Table XXIX—(See Table VIII)

$A = 12.03$

t	$A - x$	AK
10	8.51	0.0345
17	6.83	0.0333
23	5.59	0.0333
31	4.33	0.0329
45	2.68	0.0332
60	1.57	0.0339

Average = 0.0335

$K_1 + K_2 = 0.0336$

Table XXX—(See Table XVII)

$A = 5.92$

t	$A - x$	AK
8	3.33	0.0633
16	1.92	0.0707
21	1.42	0.0691
27	0.93	0.0690
33	0.61	0.0690
41	0.38	0.0670
54	0.12	0.0721

Average = 0.0686
$K_1 + K_2$ = 0.0685

Table XXXI—(See Table XVIII)

$A = 5.93$

t	$A - x$	AK
15	2.22	0.0654
21	1.50	0.0654
26	1.07	0.0659
32	0.71	0.0663
38	0.49	0.0656
50	0.20	0.0677

Average = 0.0660
$K_1 + K_2$ = 0.0661

Benzonitrile and Benzimido Ethyl Ester

Benzimido ethyl ester hydrochloride was prepared by the method described by Pinner[1] with modifications.[2] A mixture of one mole of benzonitrile and 1.25 moles of alcohol (containing not more than 0.06 per cent. water) was treated with 1.50 moles of dry hydrochloric acid gas. While the gas was being passed in, the mixture was kept in crushed ice. After standing in the cold several hours, the solution was treated with a few crystals of the benzimido ethyl ester hydrochloride to induce crystallization and allowed to stand forty-eight hours, when it became a solid mass. This was then thrown on a filter and washed with cold alcohol and ether. It was then placed in a vacuum desiccator over calcium oxide and

[1] Die Imidoäther (1892), p. 53.
[2] Marshall and Acree: Am. Chem. J., **49**, 134.

after twenty-four hours was analyzed. The yield varied from 65 to 100 per cent. The following are some typical analyses:

0.5301 gram substance gave 0.4096 gram AgCl.
0.7632 gram substance gave 0.5911 gram AgCl.
0.6166 gram substance gave 0.4777 gram AgCl.
0.6194 gram substance gave 0.4790 gram AgCl.

Per cent. chlorine,	
Found	Theoretical
19.11	19.10
19.16	.....
19.15	.....
19.12	.....

Benzimido Ethyl Ester.—As considerable difficulty was experienced in preparing pure benzimido ethyl ester by the ordinary method[1] and in keeping it pure, the following method was tried.

To an alcoholic solution of benzimido ethyl ester hydrochloride was added exactly the molecular equivalent of sodium ethylate. The sodium chloride was filtered off and the solution was distilled *in vacuo*. After several distillations a constant boiling substance was obtained, but it contained some free benzonitrile as was shown by the reaction velocity. Therefore, all solutions of the imido ester were prepared from an alcoholic solution of its hydrochloride and sodium ethylate as described under the acetimido ethyl ester.

I first proved that the free imido ester does not decompose with any appreciable velocity unless catalyzed by the ethylate. A solution of the benzimido ester hydrochloride wates tread with nine-tenths of the theoretical amount of ethylate and titrated at intervals.

Time	2 hrs.	3 hrs.	22 hrs.	45 hrs.	72 hrs.	7 days	10 days	15 days	19 days
Cc. 0.2 N HCl	10.94	11.00	10.96	10.94	10.96	10.70	10.52	10.20	10.00

The amount of change due to the *uncatalyzed*, or spontaneous, decomposition of the free imido ester cannot produce any appreciable error in our constants. When portions of this

[1] Derby: Am. Chem. J., **39**, 442 (1908).

solution were treated with N/8 sodium ethylate the imido ester was decomposed as usual.

Hydrolysis Correction.—In working with this compound hydrolysis was so marked that it was necessary to correct for it. This was accomplished in the following way: Amounts of benzimido ethyl ester hydrochloride dissolved in 10 cc. alcohol, corresponding to various stages in the reaction of a 0.25 N solution, were put in Nessler comparison tubes and diluted to 100 cc. with water, two drops of methyl orange being added to each tube. To another series of tubes containing 10 cc. alcohol, 90 cc. water and two drops of methyl orange were added 0.01 N hydrochloric acid till the colors matched those produced by hydrolysis in the first series.

The following table gives the amounts of 0.01 N hydrochloric acid necessary to produce this color:

Weight imido ester hydrochloride	Cc. of 0.01 N HCl	Corrected for blank
0.9280 g.	1.4	1.0
0.7424	1.2	0.8
0.4640	1.1	0.7
0.2774	0.8	0.4
0.1856	0.5	0.1
0.0928	0.4	0.0
0.0000	0.4	...

The following table gives corrections applied to the titrations at time periods corresponding to various values of x. These were subtracted from the values of x actually observed:

x	Correction in cc. 0.2 N HCl
0.00	0.05
2.50	0.04
6.25	0.03
8.75	0.02
10.00	0.01
12.50	0.00

Table I[1]*—0.25 N Benzonitrile, or Imido Ester, and Sodium Ethylate*

Concentration sodium ethylate	Per cent. imido ester at equilibrium	
	From nitrile	From imido ester
0.75	9.28	....
0.25	9.12	....
0.125	9.52	....
0.125	9.60	9.44 9.12
0.0625	9.86	9.76 9.60
0.03125	9.70	9.12
0.015625	9.62	9.68

Table II—0.50 Sodium Ethylate and Benzonitrile

Concentration benzonitrile	Per cent. imido ester formed
0.5 N	7.60
0.5 N	7.72
0.375 N	8.37
0.25 N	9.06
0.125 N	11.12
0.0625 N	14.08
0.03125 N	14.10

Table III—0.25 N Benzimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 12.50$	$A_2 = 0$	$K = 10.0$
t	x	K_V
41	4.82	0.0135
51	5.69	0.0136
61	6.35	0.0134
94	8.06	0.0133
119	8.93	0.0129
132	9.32	0.0130
∞	11.36	.....
		Average = 0.0133
		$K_n = 0.1064$

[1] Tables I and II are taken from another article by Marshall and Acree: Am. Chem. J., **49**, 136, 138.

Table IV—0.25 N Benzimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 12.50$	$A_2 = 0$	$K = 9.59$
t	x	K_V
30	3.85	0.0139
42	4.86	0.0133
51	5.54	0.0132
63	6.33	0.0130
95	8.01	0.0129
125	9.07	0.0129
156	9.82	0.0129
∞	11.32	.....
		Average = 0.0132
		$K_n = 0.1056$

Table V—0.25 N Benzimido Ethyl Ester and 0.0625 N Sodium Ethylate

$A_1 = 12.50$	$A_2 = 0$	$K = 9.25$
t	x	K_V
60	3.77	0.0677
100	5.55	0.0677
110	5.90	0.0672
125	6.42	0.0672
141	6.88	0.0668
∞	11.28	.....
		Average = 0.0673
		$K_n = 0.1077$

Table VI—0.25 N Benzimido Ethyl Ester and 0.0625 N Sodium Ethylate

$A_1 = 12.50$	$A_2 = 0$	$K = 9.42$
t	x	K_V
60	3.82	0.0686
80.5	4.73	0.0672
105	5.68	0.0666
121	6.30	0.0675
140	6.85	0.0666
162	7.43	0.0661
∞	11.30	.....
		Average = 0.0671
		$K_n = 0.1074$

Table VII—0.25 N Benzimido Ethyl Ester and 0.03125 N Sodium Ethylate

$A_1 = 12.50$	$A_2 = 0$	$K = 9.97$
t	x	K_V
72	2.56	0.00355
102	3.35	0.00343
118	3.81	0.00345
141	4.34	0.00341
170	4.97	0.00339
213	5.78	0.00334
233	6.11	0.00332
∞	11.36	.....

Average = 0.00341
K_n = 0.1091

Table VIII—0.25 N Benzimido Ethyl Ester and 0.015625 N Sodium Ethylate

$A_1 = 25.00$	$A_2 = 0$	$K = 9.33$
t	x	K_V
100	3.67	0.00177
124	4.63	0.00184
140	5.03	0.00179
160	5.55	0.00176
180	6.18	0.00177
1260	19.74	0.00164
∞	22.58	.....

Double portions used.

Average = 0.00176
K_n = 0.1126

Table IX—0.25 N Benzimido Ethyl Ester and Sodium Ethylate

Concentration sodium ethylate	K_V	K_n
0.125 N	0.0133	0.1064
0.0625 N	0.00672	0.1075
0.03125 N	0.00341	0.1091
0.015625 N	0.00176	0.1126

Table X—Calculated Values of K_i and K_m

	Ki	K_m
V = 8 : 16	0.1090	0.1016
V = 8 : 32	0.1154	0.1007
V = 8 : 64	0.1193	0.0981
V = 16 : 32	0.1161	0.0989
V = 16 : 64	0.1204	0.0955
V = 32 : 64	0.1227	0.0906
Average,	0.1172	0.0976

Table XI—"K_n Found" and "K_n Calculated" for 0.25 N Benzimido Ethyl Ester and Sodium Ethylate

Concentration sodium ethylate	"K_n calculated"	K_n found"	Error in per cent.
0.125 N	0.1053	0.1064	+1.00
0.0625 N	0.1070	0.1075	+0.46
0.03125 N	0.1089	0.1091	+0.18
0.015625 N	0.1109	0.1126	+1.5
		Average error,	+0.78

These experiments show conclusively that the velocity of decomposition of benzimido ethyl ester by sodium ethylate can be expressed as a function of both the *concentration of the ethylate ions* and the *concentration of the nonionized sodium ethylate.* The two following tables show that sodium iodide produces a "salt effect" which is practically identical with that calculated in the manner described on page 15, by the use of our theory:

Table XII—0.25 N Benzimido Ethyl Ester, 0.0625 N Sodium Ethylate and 0.0625 N Sodium Iodide

A_1 = 12.50 Cor. for NH_3 = 0 A_2 = 0 K = 9.5

t	x	K_V
0	...	.....
73	4.30	0.00654
98	5.36	0.00654
121	6.16	0.00649
150	7.06	0.00652
166	7.50	0.00656
∞	11.30	
	Average	= 0.00653
	Calculated	= 0.00669

0.25 N Benzonitrile, 0.0625 N Sodium Ethylate and 0.0625 N Sodium Iodide.—Ten cc. required 3.12 cc. 0.2 N hydrochloric acid at first and 4.22, 4.23, 4.23 cc. at equilibrium. This corresponds to 8.8 per cent. imido ester present at equilibrium.

Table XIII—0.25 N Benzimido Ethyl Ester, 0.125 N Sodium Ethylate and 0.125 N Sodium Iodide

$A_1 = 12.41$ Cor. for $NH_3 = 0.09$ $A_2 = 0$ $K = 12.05$

t	x	K_V
40	4.63	0.0129
55	5.79	0.0128
77	7.06	0.0124
100	8.12	0.0123
110	8.71	0.0129
124	8.97	0.0125
∞	11.46	.....
	Average =	0.0127
	Calculated =	0.0131

0.25 N Benzonitrile, 0.125 N Sodium Ethylate and 0.125 N Sodium Iodide.—Ten cc. required 6.29 cc. 0.2 N hydrochloric acid at first and 7.41, 7.38, 7.39 cc. at equilibrium. This corresponds to 9.0 per cent. imido ester present at equilibrium.

CONCLUSIONS

The experimental work and theoretical discussion in the preceding pages show that ethylates accelerate in a *purely catalytic* way the decomposition of imido esters into nitriles and alcohols and the addition of alcohols to nitriles; the velocity of the noncatalyzed reaction is so small that it can be entirely neglected. By a comparison of the reaction velocities and the conductivity data it is seen that the ethylate ions have a definite influence on the reaction which is a simple function of their concentration. The nonionized sodium ethylate, furthermore, has a definite effect on the reaction velocity which can be expressed as a simple function of the concentration of the molecules. I refer all data to the normal solution and use the expression K_i for the effect of a gram equivalent of the ethylate ions, and the expression K_m for the quantitative

action of a gram equivalent of the sodium ethylate molecules, and find practically constant values for K_i and K_m, whatever the concentration of the ethylate. For benzonitrile and benzimido ethyl ester the value $K_i : K_m = 0.1172 : 0.0976$ was found, while for acetonitrile and acetimido ethyl ester the values $K_i : K_m = 0.344 : 0.228$ were obtained.

This work proves that the purely catalytic action of sodium ethylate on the decomposition of imido esters is exactly analogous to the reaction of alkyl halides with sodium, potassium and lithium ethylates, with sodium, potassium and lithium phenolates, and with sodium 1-phenyl-3-thiourazole. In all of these cases the velocity of the reaction can be expressed as a function of the concentration of the ions increased by a function of the concentration of the nonionized molecules.

The important "salt effect," noted in so many reactions when salts are added, has been studied in all of the cases discussed and proved to be due *chiefly* to a change of the concentrations of the ions and molecules demanded by the Arrhenius theory of isohydric solutions. Small subsidiary effects may be due to the greater or smaller reactivity of double compounds formed, and to physical changes in the solution, such as variations in viscosity, double salts, ionization and electronic phenomena.

The investigation is being continued to learn if the same value for K_i is obtained by the use of potassium and lithium ethylates. The important subject of "salt catalysis" is one of the chief objects of these researches.

BIOGRAPHY

Julia Peachy Harrison, daughter of Peachy Gessner and Julia Riddick Harrison, was born April 30, 1886, in Richmond, Virginia. Her preparatory training was obtained in the public schools of that city and she graduated from John Marshall High School in February, 1904. She then entered Richmond College, receiving the degrees of Bachelor of Arts, Master of Arts and Bachelor of Science in 1906, 1907, and 1909, respectively. During the year of 1907–08 she taught chemistry at John Marshall High School and during the year 1908–09 was laboratory assistant in chemistry at Richmond College. In October, 1909, she entered Johns Hopkins University as a graduate student in chemistry with physical chemistry and physics as subordinate subjects.